Development of Schiff Base Chemosensor from Citrus Fruit Waste for Detection of Metal Ions in Contaminated Water

SHORT SYNOPSIS

Submitted in partial fulfillment of the requirement of the degree of

DOCTOR OF PHILOSOPHY

by

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DECLARATION BY THE SCHOLAR

I hereby declare that the short synopsis entitled "**Development of Schiff Base Chemosensor from Citrus Fruit Waste for Detection of Metal Ions in Contaminated Water**" being submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the **Department of Sciences (Chemistry)** under the **School of Sciences** of **Manav Rachna University, Faridabad** during the academic year 2024-25.

It is the work that is expected to be carried out under the supervision of Prof. (Dr.) Sangita Banga, and co-supervision of Dr. Vinayak V. Pathak.

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This is to certify that, the short synopsis entitled "**Development of Schiff Base Chemosensor from Citrus Fruit Waste for Detection of Metal Ions in Contaminated Water**" is an original piece of work done by research scholar Eksha Guliani under the supervision of Prof. (Dr.) Sangita Banga and co-supervision of Dr. Vinayak V. Pathak for the degree of Doctor of Philosophy in the **Department of Sciences (Chemistry)** under the **School of Sciences** of **Manav Rachna University, Faridabad** during the academic year 2024-25.

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ABSTRACT

In present investigation, efforts will be made to synthesize a novel citrus fruit waste based chemosensor by integrating it with amino acid derivatives. The procured citrus fruit waste biomass will undergo a pre-treatment process for optimization of extracted platform molecules by following the experimental data set obtained from Response Surface Methodology (RSM). For the derivatization of procured platform molecules, heterogeneous catalysts will be synthesized to carry out the oxidation process. The as-synthesized heterogeneous catalysts will be characterized by UV, FTIR and XRD techniques in order to study their optical behavior, nature of bonding and phase determination respectively along with its physiochemical behavior. The obtained platform molecule derivative will undergo a reaction with amino acid derivatives to form Schiff base and the completion of reaction will be monitored by Thin Layer Chromatography or GCMS. The synthesized Schiff base will act as a chemosensor that will be tested for its sensing ability for selected metal ions and initializing their entrapment inside the cavity due to synergistic effect. The structural aspects of the chemosensor will be confirmed by UV, NMR, FTIR, GCMS and LCMS characterization techniques. Further, the residue remaining after extraction will be subjected towards the formation of various value-added products. Thus, the present investigation provides a cost-effective and a sustainable approach for synthesis of desired chemosensor in order to detect metal ions from contaminated water while focusing on zero waste production.

Keywords: Amino acid; chemosensor; citrus fruit waste; fluorescence; heterogeneous; Schiff base

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1. INTRODUCTION

A chemosensor is basically defined as a miniature device that possesses the ability of detecting a targeted substance by showing the response in terms of energy change. This miniature device is composed of four basic components as shown in figure 1. First, is an analyte which is that ion/atom/molecule which needs to be detected. Second, is the sensing element or receptor which particularly binds with the analyte of interest. Third, is a transducer that converts the emitted signals into optical or electrical signals which are smoothly detected by the fourth component; detector. Finally, the display shows the detected signals in the form of graphs which is interpreted by the user on the other end. Chemosensor is a versatile device which possesses potent applications in almost every field like it is widely utilized in environmental monitoring, medical diagnostics, food safety, agriculture, forensic science, wearable technology, military and defense, drug development, etc. (Guliani et al., 2023).

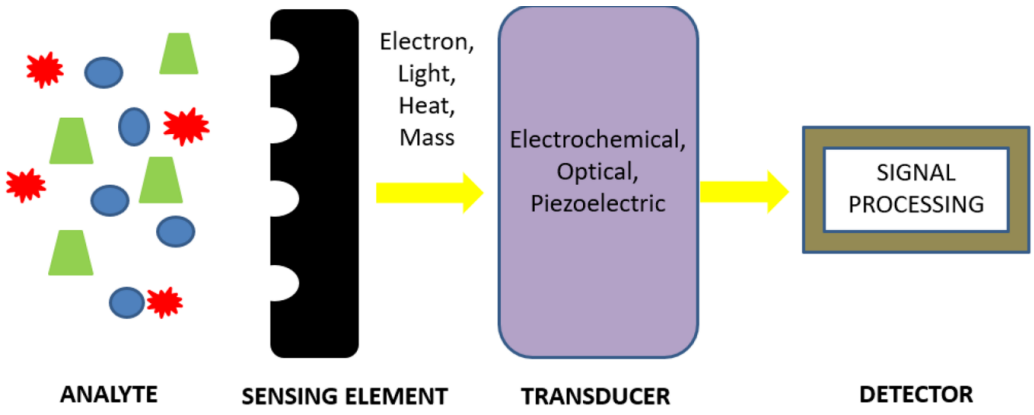


Figure 1: Representation of basic components of a chemosensor.

The first fluorescent chemosensor was initially invented in 1867 by Friedrich Goppelsroder. He proposed a method for determination of Al^{+3} ions using a fluorophore. After this, researchers have prominently worked for the development of chemosensors which eventually led to the evolution of analytical chemistry. Later in the year 1980, Anthony W. Czarnik, Roger Tsein and A. Prasanna de Silva have led developed luminescent probes for ions detection that were present in the biological cells. Roger Tsein further improvised the study by developing green fluorescent proteins and was awarded with the Nobel Prize for the same in 2008. Lynn Sousa led to the discovery of

alkali metal ions detection via fluorescent sensing by utilizing supramolecular chemistry along with the coworkers J.M. Lehn and H. Bousa-Laurent in France. Also, L. Fabbrizzi have led to transition metal ions detection by photoinduced electron transfer (PET) sensing mechanism. This pioneering development of chemosensor has greatly influenced the scope of advancements in the field of science and technology by causing a selective detection of ions or molecules by recording the observable changes (Kwon et al., 2018).

The detection of metal ions from the environment is very much important because of their toxic effects. If these metal ions are present beyond their permissible limit, their exposure could lead to severe health problems like kidney disease, neurological damage, etc. and can even cause ecological damage by contaminating the air, water and soil. The increase in industrialization and urbanization has led to a rapid growth in activities like mining and manufacturing which are the primary source of release of toxic metal ions into the environment. So, detection of metal ions has elevated its importance in the field of environment which can vary upon the chosen selected geographical location. For example, if high levels of copper metal ion are present in drinking water, it can lead to some gastrointestinal issues with acute poisoning. Elevated concentration of zinc metal ion can lead to nausea, diarrhea and vomiting. A long-term exposure to the aluminium metal ion can lead to cognitive impairments and neurological disorders. Therefore, research is mandatory to be carried out in order to isolate and detect toxic metal ions that act as a pollutant to both biotic and abiotic resources of nature.

Citrus fruits basically represent about 98% of the industrial crops out of which 82% is composed of oranges. The overall production of citrus fruit is recorded for about 158.49 million MT in which Asia is regarded as the highest producing citrus fruit content of about 47.7%. About 10.07 million hectares of land is occupied for citrus fruits production which is led by China, India, Nigeria and Brazil. Citrus belongs to Rutaceae family which is rich in various bioactive components and phytochemicals like flavonoids, terpenes, etc. It has a huge consumption because of its appealing fragrance, taste and nutritional values. The waste produced from citrus peels is about 50% of the total citrus fruit weight in general. About 2.59 billion tons is predicted to be produced by the year 2030 which could even reach to 3.4 billion tons by the year 2050 (Suri et al., 2022). The improper disposal of the waste produced from citrus fruits is the main cause of greenhouse gas emission and

the easiest disposal routes out of all is landfill because of the ease of implementation. Therefore, disposing the segments of citrus waste is creating an unnecessary burden for environment because of the unhygienic and undesirable nature. A proper utilization of such waste might serve as a renewable means in order to recover various bio-based products that would eventually reduce the environmental problems.

Essential oils are lipophilic molecules which possess very low or negligible solubility in water. These are composed of various volatile components which are basically found in the cuticle of plants. These are used as flavoring agents in food industry in order to add a citrus flavor in food and beverages. They even have a wide range of application in pharmaceutical industry and cosmetic industry as they add fruity fragrance to perfumes, soaps and other products. Monoterpenes are the basic building blocks that provide aroma and flavor to the substance from which it has been extracted. These even possess anti-inflammatory, anti-anxiety, anti-oxidant and anti-carcinogenic activities which operate at both molecular and cellular level. D-limonene is a monoterpene which is chemically named as 1-methyl-4-(1-methylethenyl) cyclohexene and is a colorless liquid with a citric odor but can result in various skin allergies if prolong contact is made. Its maximum concentration is present in the orange peels and is used as an additive in beverages, cosmetic products, insect control, etc. D-limonene is soluble in organic solvents like alcohol and ethers but is insoluble in water (Kvittingen et al., 2021).

Amino acids are the building blocks of human body. When these are combined in sequence, they form proteins to perform a myriad of various functions in human body. The derivatives of amino acids act as precursors to various hormones and also as critical biomolecules in the formation of metabolic intermediates. These have diverse functions which underline their versatility by causing a balance in physiological homeostasis. Therefore, in the proposed research methodology, amino acid derivatives will be combined with the citrus fruit waste derived platform molecule to form a Schiff base that will orient itself in such a way that induces cavity. This will form the basic framework of the desired chemosensor which will also show some antimicrobial activity. Therefore, proposed research in the field of bioprocessing of citrus fruit waste biomass for development of a chemosensor holds a great significance in the present scientific landscape.

2. LITERATURE REVIEW

2.1 Extraction of Platform Molecules from Waste Biomass

Platform molecules are basically those organic moieties that are derived from waste biomass and these can be utilized as building blocks for producing high commodity refined chemicals. These molecules possess several applications and are a vital part of drug development in pharmaceutical industry. Waste biomass consists of a complex structure having lignocellulosic content which hinders the release of compounds from the cells. The pre-treatment method possesses the ability to weaken the cell walls in order to release essential oil from the oil glands of fruit waste. Therefore, this arises the need for pre-treatment of waste biomass before carrying out extraction. Some pre-treatment methods include thermal shock, ultrasonication, acid and alkaline pre-treatment, enzymatic hydrolysis, fermentation, microwave-assisted pre-treatment, etc. The extraction of platform molecules is an upstream process and few methods have been discussed to isolate them from waste biomass in table 1 and their structures are shown in figure 2.

Lifeng et al. have carried out the extraction of levulinic acid from wheat straw having 40.4% of cellulose content. The procured biomass was mixed with 4.5% HCl to form a suspension and then liquified at 220^0C in water for about 45 mins in a pressurized steel reactor. After the completion of reaction, the mixture was directly analyzed to study the chemical composition by HPLC method. It resulted in 23.7% of levulinic acid along with some other compounds as per the analysis recorded by linear regression statistics (Yan et al., 2008).

Yadhu et al. have extracted 2,3-butanediol from sorghum stalk biomass by first pretreating it by alkali treatment process and then autoclaving it at 121^0C for about 30 mins. The slurry obtained was hydrolyzed enzymatically by using *Bacillus licheniformis* DSM 8785 in a citrate buffer that eventually produced sugar concentrations. 2,3-butanediol production was feasible in single-sugar medium by releasing 103 g/L of its total quantity upon fermentation as recorded by the statistical analysis (Guragain et al., 2017).

Khanitta et al. have utilized *Moringa oleifera* (drumstick seeds) to produce oleic acid platform molecule which is a monounsaturated fatty acid. They have followed supercritical fluid extraction (SFE) method by using CO_2 as a solvent which is a green synthesis method. The optimum extraction was carried out at a fixed flow rate of 20 kg/h, at a pressure of 35 MPa and moderate temperature of 35^0C. The product obtained was effectively characterized by GCMS which revealed

that the isolated oil content contained 72.26% of oleic acid (Ruttarattanamongkol et al., 2014).

Graziane et al. have extracted tocopherol from *Heliantus annuus L.* (sunflower seeds) via soxhlet extraction by using propane and n-hexane as solvent. The optimum conditions recorded for the experiment were at a temperature of 60^0C for 40 mins. The kinetics of extracted oil was described by Sovová model and the followed methodology led to the production of 0.41 kg oil/kg from seeds with 0.195 mm as Sauter particle size. The characterization techniques revealed that the obtained oil contained, when extracted using n-hexane produced a maximum quantity of tocopherol which is widely known as vitamin E (Nimet et al., 2011).

Rui M.A. et al. have extracted ursolic acid from eucalyptus bark which is a bioactive triterpenoid. The extraction from the waste biomass was processed by comparing the yield obtained from supercritical fluid extraction (SFE) methodology using CO_2 and soxhlet extraction in dichloromethane. It was observed that at a pressure of 160 bar and temperature of 40^0C, a threefold increase in the yield was noted upon the addition of 8% ethanol to the solution. About 2.77 g/kg of oil was obtained and then characterized by GCMS which revealed the maximum concentration of ursolic acid along with some acetyl derivatives by SFE method (Domingues et al., 2012).

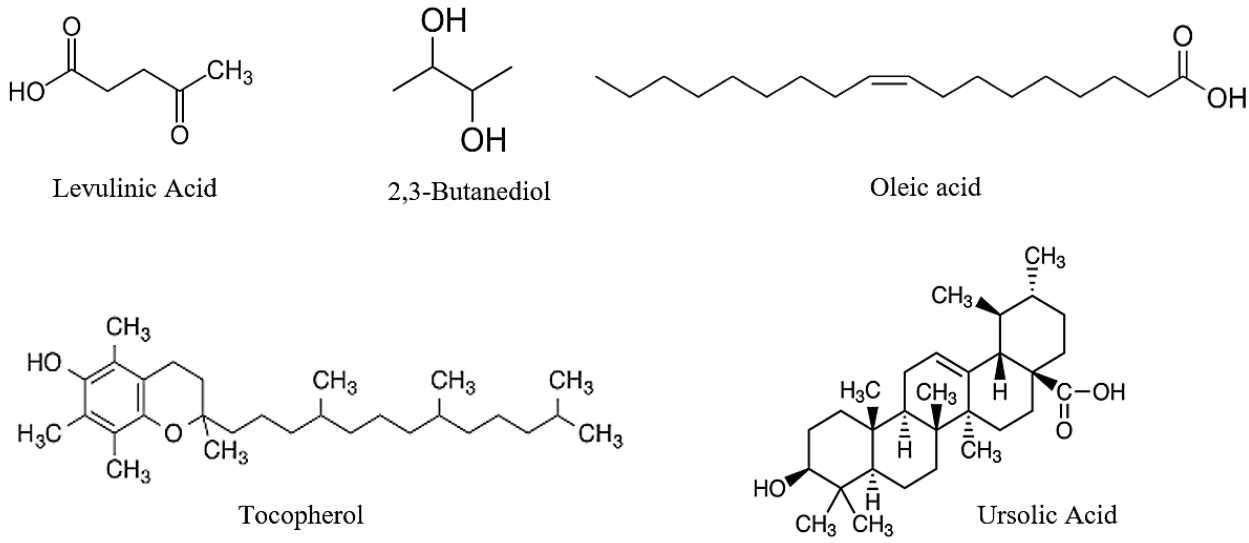


Figure 2: Structures of platform molecules isolated from waste biomass.

Table 1: Summary of platform molecules extracted via different extraction techniques.

S.No.	Waste Biomass	Platform Molecule Extracted	Extraction Process	Optimum Conditions	Yield Recorded	Reference
1	Wheat straw	Levulinic acid	HPLC Method	220^0C, 45 mins	23.70%	Yan et al., 2008
2	Sorghum stalk	2,3-Butanediol	Enzymatic hydrolysis	121^0C, 30 mins	103 g/L	Guragain et al., 2017
3	Drumstick tree	Oleic acid	Supercritical fluid extraction	35 MPa, 35^0C, flow rate 20 kg/h	72.26%	Ruttarattanamongkol et al., 2014
4	Sunflower seeds	Tocopherol	Soxhlet extraction	60^0C, 40 mins	0.41 kg oil/kg	Nimet et al., 2011
5	Eucalyptus bark	Ursolic Acid	Supercritical fluid extraction	160 bar, 40^0C	2.77 g/kg	Domingues et al., 2012)

2.2 Extraction Methods

The platform molecules from the waste biomass can be commonly extracted by steam distillation, cold pressing or soxhlet extraction methods. These strategies of extraction have certain drawbacks like long extraction period, polar components loss as well as less yield of product. They even involve the utilization of various solvents that eventually hampers the environment when disposed in sinks. The proposed research methodology has advantages over the conventional extraction methods as summarized in table 2.

Table 2: Comparison of existing extraction methods with proposed methodology.

S.No.	Existing State of Art	Drawbacks in Existing Methodologies	Proposed Methodology
1	Cold pressing	Low yield, slow process, quality issues, storage problem, variation in reproducibility, limited to certain materials, utilization of solvents	Higher yield, fast process, high quality, reproducible, solvent free extraction
2	Soxhlet extraction	Time consuming, utilization of large quantity of solvents, low efficiency, product might degrade, extraction of several compounds	Less time, no solvent utilization, high efficiency, degradation depends on nature of product, only required compound co-distilled with water
3	Carbon-dioxide extraction	High investment for setup, complex, higher utilization of energy, cannot be scaled, selective extraction, concern regarding safety, challenge in product quality	Low investment for setup, less energy utilization, easy to operate, has been optimized, only PPEs required for extraction, higher product quality
4	Enfleurage	Labor required in large number, low yield, limited to certain materials, temperature sensitive, limited shelf-life, time consuming, high cost, impact the environment	No specific labor required, higher yield, longer shelf life, environment friendly, low cost
5	Maceration	Time consuming, inefficient, limited, low yield, use of large quantity of solvents, impact the environment	Less time consuming, efficient, higher yield, solvent free, environment friendly

2.3 Fluorescence Based Chemosensor

Fluorescence phenomenon involves the absorbance of light with particular wavelength by a molecule. This results in the excitation of electron from its ground state to excited state. The excited electron then immediately returns back to its ground state by emitting light which is termed as fluorescence. This technique is a widely utilized technique that is capable of detecting the entrapment of metal ions in the cavity of chemosensors. Due to emission and absorption of energy by excited electron, there is one fluorophore that is the center of energy donor whereas the other one behaves as an energy acceptor resulting in some intermolecular transfer of energy.

The chemosensors based on fluorescence phenomenon basically includes an interaction among the binding site and the guest compound resulting in the electronic changes as exhibited by the generation of a fluorescent signal. This detection technique has many advantages over other techniques like it is highly sensitive and selective with low-cost of instrumentation setup. This particular technique can be combined with some other technique like microscopy which enables the analyte's detection with a higher and clear resolution. If the fluorescence intensity gradually increases upon the detection of analyte, then it is termed as a turn-on fluorescent chemosensor whereas a gradual decrease in the fluorescence intensity upon the detection of analyte makes it a turn-off fluorescent chemosensor. Also, if the chemosensor changes its color upon detection of analyte, it is termed as a chromogenic chemosensor.

According to the Jablonski diagram in figure 3, photon is absorbed by a molecule which leads to its movement towards excited state (S_0 to S_1) and later relaxes to its lowest vibrational level (S_0) by emitting a lower energy photon of a longer wavelength (Stokes Shift). A molecule in its ground state (S_0), absorbs in UV-visible region which is then excited to its higher electronic state (S_1). The fluorescence efficiency is completely influenced upon the quickness of a molecule that possesses the ability to emit a photon before undergoing intersystem crossing (S_1 to T_1) or a non-radiative decay which can lead to phosphorescence phenomenon. The Jablonski diagram clearly explains that fluorescence is a short-lived phenomenon as it occurs immediately after the excitation has taken place in a molecule.

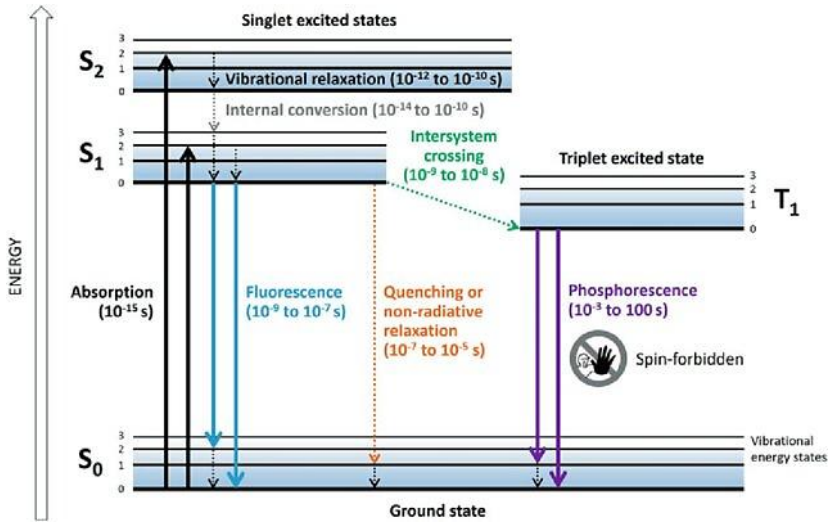


Figure 3: Jablonski diagram explaining the phenomenon of fluorescence and phosphorescence.

2.4 Formation of Chemosensor Framework from Isolated Platform Molecules

The synthesis of chemosensor is a downstream process and some examples of the synthesis of chemosensors have been discussed as follows along with its application as in figure 4.

Liping et al. have efficiently synthesized poly(ethylene) glycol which was a Schiff based furan chemosensor having solubility in water. Initially, furan-2-carbohydrazide and dihydroxybenzaldehyde were refluxed (under nitrogen atmosphere) for 2 h. Then the reaction mixture was dried and left overnight to obtain a light pink colored precipitate. The synthesized chemosensor exhibited a strong selectivity towards Al^{+3} ions with a strong excitation at 369 nm, limit of detection as 7.90×10^{-9} M at a pH between 5-9 which eventually changed its color to bright cyan upon detection (Bai et al., 2020).

Atika et al. have synthesized a quinoline based chemosensor possessing ability to trap Cu^{+2} ions in the cavity with a stoichiometry of 1:1. A methanolic solution of phthalic dicarboxaldehyde and 8-aminoquinoline was refluxed at 80^0C for 72 hours. It led to the appearance of an orange colored precipitate which was then filtered and washed with toluene to remove impurities which was further vacuum dried. A bright colored fluorescence was recorded which showed a bathochromic shift of 35 nm and at a pH range of 6-9 with limit of detection as 1.03 µM (Farhi et al., 2019).

Yi et al. have formulated a chemosensor which was carbazole based. It was capable of trapping Fe^{+3} ions into the cavity by showing 15 seconds of response time. The synthesis of the desired

chemosensor was a three step synthesis reaction. In the latter stage, the mixture of 9-hexyl-9H-carbazole-3-carbaldehyde and 2,3-diaminomaleonitrile was refluxed in ethanol for 7 h at 70^0C. The residue obtained was the desired product that was a double Schiff base product. Upon addition of Fe^{+3} ions, the fluorescence was quenched at 280 nm and its limit of detection was 3.75×10^{-8} M (He et al., 2018).

Ju Byeong et al. have effectively synthesized fluorescent based chemosensor having quinoline as a heterocyclic moiety possessing the ability to detect Zn^{+2} ions. It has shown a prominent response with limit of detection as 0.27 µM. For carrying out the synthesis, 2-chloro-N-(quinolin-8-yl)acetamide and 2,2′-(ethane-1,2- diylbis(oxy))bis(ethan-1-amine) were dissolved in acetonitrile with a few drops of triethylamine. The reaction mixture was then refluxed for 2 days which led to the formation of a brownish oil after vacuum distillation. The chemosensor had a working pH of 3-8, which showed an excitation at 343 nm (Chae et al., 2019).

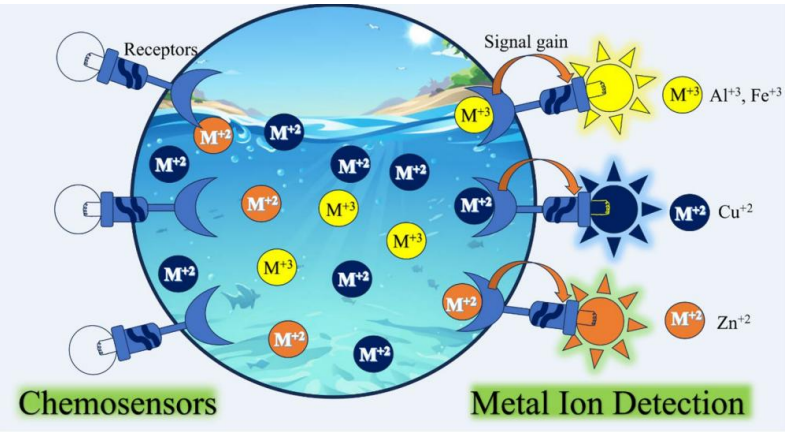


Figure 4: Ability of chemosensor to detect the metal ions from contaminated water.

2.5 Applicability of Chemosensor in Real-life

Chemosensors play a very vital and a critical role in environment monitoring. These are portable devices which enables real-time monitoring, provide a quick response, cost-effective, selective, sensitive and can detect pollutants even at very minute concentrations. Some of the key applications of this versatile material is discussed as follows:

1. Environmental Monitoring:

   Detection of metal ions in water: Fluorescent chemosensors are designed in such a way that they possess the ability to detect metal ions in the water that causes contamination.

Analysis of soil health: Chemosensors are able to detect the presence of any foreign invasive particles that hampers the fertility of soil.

2. Food Security and Quality Assurance:

   Detection of pathogens: The presence of some pathogens like *E. Coli* and *S. Aureus* in food can be detected via the use of chemosensors.

   Adulteration monitoring: The presence of adulterants like melamine in food items can be identified by utilizing chemosensors.

3. Defense and Security:

   Detection of explosives: The explosives like RDX or TNT if present in traces can be identified by the application of chemosensors in forensic screening and investigations.

   Illicit drug detection: The utilization of chemosensors at ports and borders helps in the detection of narcotics in order to compact the trafficking of drugs.

4. Electronic Devices:

   Smartphones: The use of chemosensors in smartphones helps in tracking hydration levels and record the health diagnostics data.

   Safety at homes: Utilizing chemosensors in smart devices at homes helps in the detection of gas leakage and air quality checks.

5. Medical Diagnostics:

   Monitoring of glucose: A regular check on the level of glucose is monitored with the help of devices containing chemosensors which is very helpful for diabetic patients.

   Detection of biomarkers: Specific biomarkers can be identified by using chemosensors in body fluids which helps in the early detection of diseases.

3. DESCRIPTION OF TOPIC

The research in the field of bioprocessing of citrus fruit waste biomass for development of a chemosensor holds a great significance in the present scientific landscape. This research aims to provide an ecofriendly approach which is biocompatible with the environment. The integration of metal ions into the cavity of the Schiff base would act as a chemosensor that would be utilized in the detection of toxic metal ions by showing enhancement in fluorescence. The metal chelated complex formed would exhibit certain antimicrobial activity making it an effective antimicrobial agent.

Also, its synthetic route follows the principles of green chemistry making them a promising candidate to be utilized effectively in cosmetics industry, pharmaceutical industry, biorefinery, etc. The platform molecules are extracted from CFW making it an economical process as waste is widely available in every household on daily basis. The optimization process would involve a lot of manpower which would eventually lead to an increase in the employment sector. Therefore, the proposed methodology is significantly sustainable and economical, aiming for the betterment of the society.

4. OBJECTIVES OF RESEARCH

Based upon the challenges and gaps as discussed in literature review, following are the objectives proposed for the research work:

a) Response Surface Methodology (RSM) based optimization of extraction conditions (time and temperature) of D-limonene from citrus fruit waste (CFW) and its characterization.
b) Synthesis and characterization of heterogeneous catalyst for oxidation of D-limonene and studying its physiochemical behavior.
c) Esterification, optimization and characterization of amino acids to form amino acid methyl esters.
d) Optimization and characterization of Schiff base formation to form basic framework of chemosensor.
e) To evaluate the performance of developed chemosensor for detection of metal ions from contaminated water.

5. METHODOLOGY TO BE ADOPTED

5.1 Requirements for Synthesis Process

5.1.1 Raw Materials Required

The CFW will be collected from a local fruit vendor. The procured CFW will be washed under running water to remove any dirt particles and will be stored in fridge for further processing.

5.1.2 Chemicals and Glassware Required

There are various requirements for carrying out the synthesis process and those are mentioned in the following table 3.

Table 3: Chemicals and glassware required for the synthesis of desired chemosensor.

S.No.	Glassware/Apparatus	Chemicals	Solvents
1	Micropipette tips (1 mL)	30% Hydrogen peroxide	Acetonitrile
2	Magnetic Stirrer	Sodium Borohydride	Dichloroethane
3	Two neck round bottom flask	Selected Amino Acids	Dichloromethane
4	Nitrile Gloves	Calcium chloride	Diethylether
5	TLC Plates	Chloramphenicol	Dimethylformamide
6	Disposable Syringe	L-Carvone Standard	Dioxane
7	Ballons and Rubber Bands	D-Limonene Standard	DMSO
8	Eppendrof (1 mL)	N-Ethyldiisopropylamine	Ethanol
9	Rubber Septum (B-24)	Sodium Carbonate	Ethyl acetate
10	Microtiter Plates	Pyridinium Dichromate	Heptane
11	Glass Vial (Sample Vial)	Resazurin Dye	Methanol
12	Condenser	Metal salts (Hydrated)	Pentane
13	Hair Dryer	Potassium Permanganate	Propan-2-ol
14	Magnetic Beads	Sodium Triacetoxyborohydride	Tetrahydrofuran
15	TLC Capillary	Thionyl Chloride	Toluene
16	Sand Bath	Titanium Isopropoxide	
17	Distillation Setup	Triethyl amine (TEA)	
18	Prep TLC Plates	Zinc oxide	
19	Microfilter	Magnesium Chloride	
20	Balloon and rubber bands		

5.2 Research Methodology

5.2.1 Citrus Fruit Waste Procurement and Its Pre-Treatment:

Citrus fruit waste biomass contains very high percentage of lignocellulosic and lipid content along with some bioactive components. Before carrying out the extraction process by hydrodistillation method, the CFW will undergo a pre-treatment process as per the literature review in order to release the essential oil content from cells to enhance the yield. Also, the moisture content will be calculated (Eq. 1) for procured CFW by:

$$\text{Moisture Content}(\%) = \frac{\text{Weight of dried waste biomass}(\text{g})}{\text{Weight of wet waste biomass}(\text{g})} \text{X } 100 \qquad \text{(Eq. 1)}$$

5.2.2 RSM Based Optimization of Platform Molecules:

The optimization of the extraction process will be carried out by performing analysis via response surface methodology (RSM) using central composite design (CCD) in design expert software. Initially, the operating parameters or independent variables will be chosen that governs the extraction process. The influence of the chosen variables and their interaction with others will be analyzed by using *F*-test and analysis of variance (ANOVA). RSM will hence formulate a second order regression equation that will be used to correlate the responses by fitting the experimental data and the response variable (Y) which is the yield of essential oil. Therefore, a table will be designed for the optimization of the identified independent variables at a 5-level setting for optimization (table 4).

Table 4: Central composite design matrix for independent variables with 5-level setting.

Coded Levels	**-α**	**-1**	**0**	**1**	**+α**
Variable A					
Variable B					

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Therefore, the second order polynomial (Eq. 2) formed is:

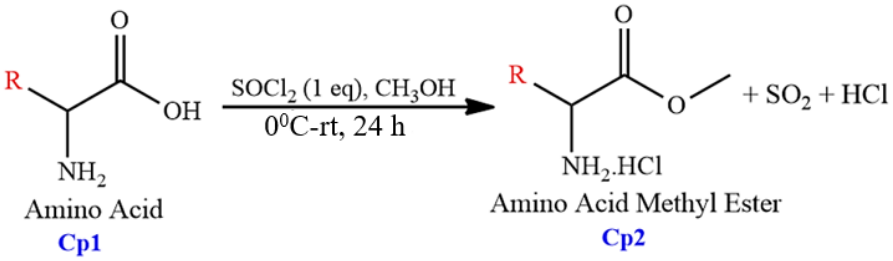
$$Y = 1.96 - 0.1422A - 0.3604B + 0.2158AB + 0.2012A^2 – 0.2503B^2 \quad \text{(Eq. 2)}$$

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings.

5.2.3 Synthesis of Amino Acid Derivatives:

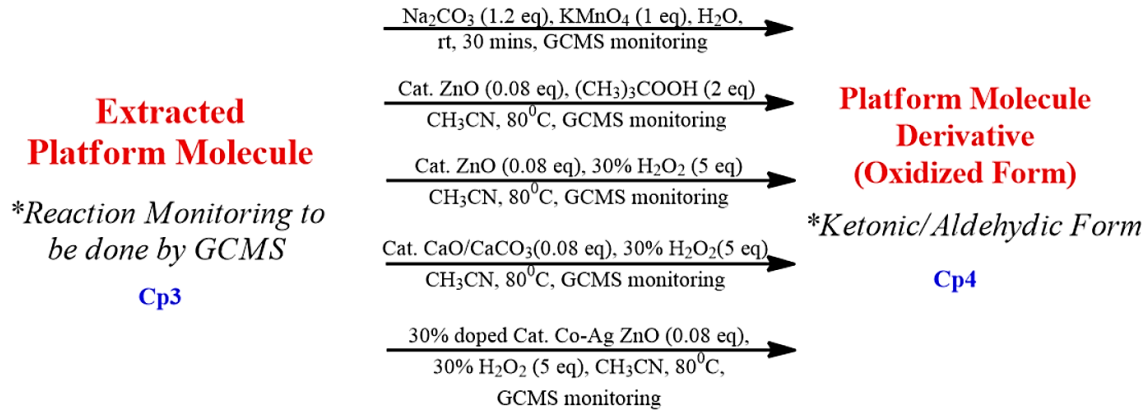
The selected amino acids will be converted into methyl esters which are prepared by dissolving the desired amino acid in methanol with thionyl chloride at 0^0C. The reaction mixture will be stirred continuously for 24 h at rt. The mixture obtained will be concentrated till its 1/4th

concentration and will be further subjected to crystallization. The crystals will be dried in an oven for further analysis and yield would be noted.



5.2.4 Synthesis of Platform Molecule Derivatives:

The procured platform molecule will be further converted into its stable form (oxidized form) by undergoing oxidation reaction. Some of the proposed synthesis are as follows:

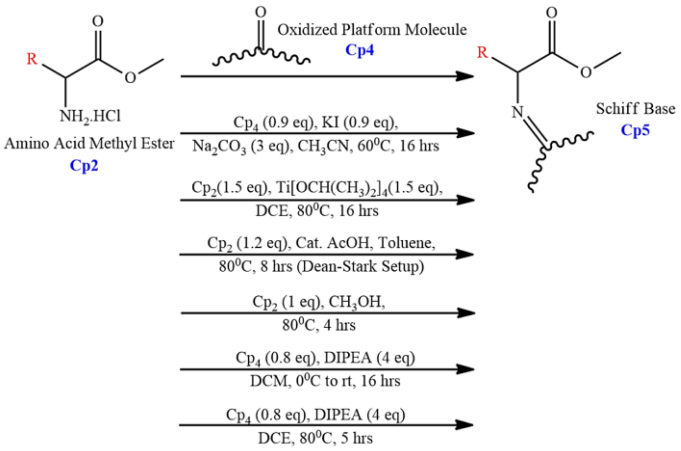

Extracted Platform Molecule
*Reaction Monitoring to be done by GCMS
Cp3
Na2CO3 (1.2 eq), KMnO4 (1 eq), H2O, rt, 30 mins, GCMS monitoring
Cat. ZnO (0.08 eq), (CH3)3COOH (2 eq) CH3CN, 80⁰C, GCMS monitoring
Cat. ZnO (0.08 eq), 30% H2O2 (5 eq) CH3CN, 80⁰C, GCMS monitoring
Cat. CaO/CaCO3(0.08 eq), 30% H2O2(5 eq) CH3CN, 80⁰C, GCMS monitoring
30% doped Cat. Co-Ag ZnO (0.08 eq), 30% H2O2 (5 eq), CH3CN, 80⁰C, GCMS monitoring
Platform Molecule Derivative (Oxidized Form)
*Ketonic/Aldehydic Form
Cp4

5.2.5 Synthesis of Heterogeneous Catalysts:

It is very well reported that the semiconductor metal oxides possess unique physical and chemical properties as they promote very rapid electronic transitions by causing photo-induced reactions. Therefore, various metal precursors will be utilized for the formation of bimetallic or trimetallic catalysts in order to increase the rate of oxidation by increasing the surface area of adsorption. The physiochemical properties of the synthesized heterogeneous catalysts will be studied along with its application in oxidation reaction of the isolated platform molecules. The heterogeneous catalyst will possess a wide band gap and good quantum efficiency.

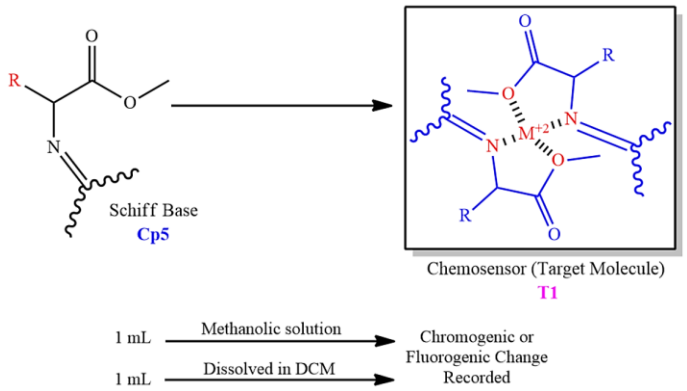
5.2.6 Formation of Chemosensor Framework:

There will be a formation of Schiff base when amino acid methyl ester will react with the platform molecule derivative as per the researches combined in literature review. Following are some proposed reaction conditions for the synthesis of Schiff base.


Oxidized Platform Molecule
Cp4
Amino Acid Methyl Ester
Cp2
Schiff Base
Cp5
Cp4 (0.9 eq), KI (0.9 eq), Na2CO3 (3 eq), CH3CN, 60°C, 16 hrs
Cp2(1.5 eq), Ti[OCH(CH3)2]4(1.5 eq), DCE, 80°C, 16 hrs
Cp2 (1.2 eq), Cat. AcOH, Toluene, 80°C, 8 hrs (Dean-Stark Setup)
Cp2 (1 eq), CH3OH, 80°C, 4 hrs
Cp4 (0.8 eq), DIPEA (4 eq) DCM, 0°C to rt, 16 hrs
Cp4 (0.8 eq), DIPEA (4 eq) DCE, 80°C, 5 hrs

5.2.7 Incorporation of Metal Ions into Cavity:

Schiff base formation will eventually introduce a cavity, inviting toxic metal ions to bind with the active sites. This step is achieved by simply dissolving the adduct in DCM and adding the salt of the desired toxic metal ion in small aliquots for laboratory testing. The chemosensor so formed will be able to exhibit a strong fluorescence in UV-Visible region and the color of fluorescence will be determined by monitoring the TLC plate under UV chamber with few spots of the synthesized chemosensor or by fluorescence spectroscopy.



The following optimum parameters in table 5 will be studied for the synthesized chemosensor as per the procedure explained in the corresponding literature.

Table 5: Calculation of optimum parameters for synthesized chemosensor.

S.No.	Optimum Parameter	Reference
1	Selectivity and sensitivity	(Kumar et al., 2024)
2	Limit of Detection	
3	Stoichiometry	
4	Binding Constant	
5	Quantum Yield	
6	Reversibility	

As the synthesized chemosensor is derived from CFW, it will show anti-microbial nature as per the anti-microbial tests which will be conducted on microtiter plates by microdilution method.

5.2.8. Characterization of the Synthesized Materials:

All the synthesized materials prepared by the above methods would be characterized by the following characterization techniques:

- ✓ *UV:* Ultraviolet-Visible spectroscopy will determine the shift in absorbance value before and after chelation of metal ions. Also, it will help to study the optical behavior and band gap values of the heterogeneous catalyst so formed.
- ✓ *FTIR:* Fourier Transform Infrared spectroscopy will confirm the presence of functional group in the platform molecule and the type of bonding in the heterogeneous catalyst.
- ✓ *XRD:* X-Ray Diffraction will determine the phase and crystallite size of the materials.
- ✓ *NMR:* Nuclear Magnetic Resonance will help in the determination of chemically non-equivalent protons in all the synthesized compounds.
- ✓ *LCMS:* Liquid Chromatography-Mass Spectrometry will determine the percentage purity of the as-synthesized compounds.
- ✓ *GCMS:* Gas Chromatography-Mass Spectrometry will reveal the compositional analysis of the as-synthesized compounds.

5.2.9 Applicability of the Synthesized Chemosensor:

A laboratory scale study will be conducted for the synthesized chemosensor to detect metal ions in contaminated water. Following metal ions as mentioned in table 6 will be tested with the

synthesized chemosensor in order to check the sensitivity and selectivity for metal ions.

Table 6: Metal ions to be tested for binding capacity by chemosensor.

S.No.	Metals (Aqueous Solution)	MW (g/mol)
1	Aluminium Sulphate	630.38
2	Ammonium Chloride	53.39
3	Arsenic (II) Sulphide	246.03
4	Barium Chloride Dihydrate	244.28
5	Cadmium Chloride Monohydrate	201.32
6	Calcium Sulphate	136.14
7	Chromium (III) Chloride	266.45
8	Cobalt (II) Chloride Hexahydrate	237.93
9	Copper (II) Chloride Dihydrate	170.48
10	Ferric Chloride	162.21
11	Lead Chloride	278.1
12	Magnesium Chloride	203.3
13	Manganese Sulphate	169.01
14	Mercuric Chloride	271.5
15	Nickel Chloride	237.69
16	Potassium Chloride	74.55
17	Silver Nitrate	169.87
18	Sodium Acetate	82.03
19	Stannous Chloride	225.63
20	Zinc Chloride	136.28

5.2.10 Fabrication of Synthesized Chemosensor:

The synthesized chemosensor will be tested for metal ion detection by following methods:

Direct loading: The chemosensor solution will be directly injected into the contaminated water to show chromogenic change at particular pH value.

Polymerization: An *in-situ* polymerization technique will be used by forming the beads of

chemosensor coated on chitosan along with sodium alginate which will be then dipped into metal contaminated water.

5.2.11 Residue-Recovery of Citrus Fruit Waste:

The bioprocessing of citrus fruit waste residue possesses potential in the branch of materials science because of its anti-oxidant, anti-microbial and anti-inflammatory properties. The existing research studies require a detailed study on those agricultural biomass waste extract that can be used for the preparation of value-added products.

6. EXPECTED OUTCOMES OF THE RESEARCH

The synthesized metal-chelated Schiff base would exhibit a characteristic property of a chemosensor as it would be capable to trap selected metal ions into its cavity. After successful completion of the project, a comprehensive report with formulated research methodologies, results and conclusions would be presented in various national and international conferences.

Also, these research findings would be formulated for various publications in the respective scientific journals. The research project is completely sustainable and benign as there will be no waste production. Also, waste biomass would be utilized for extraction of platform molecules which is once again a sustainable aspect. Therefore, this study follows the sustainable development goals (SDGs) numbered 6 (Clean water and sanitation), 7 (Affordable and clean energy), 13 (Climate action), 14 (Life below water) and 15 (Life on land). Hence, the developed schematic pathway could be optimized on a large scale.

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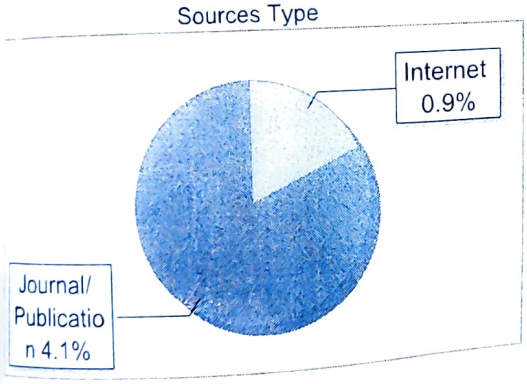

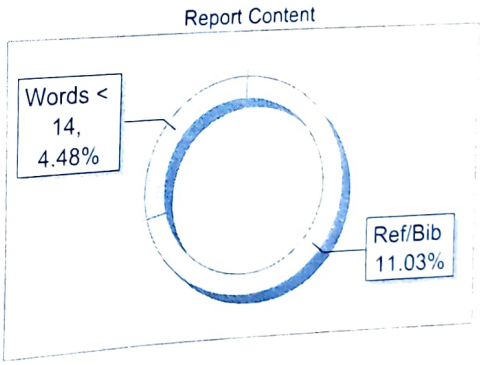

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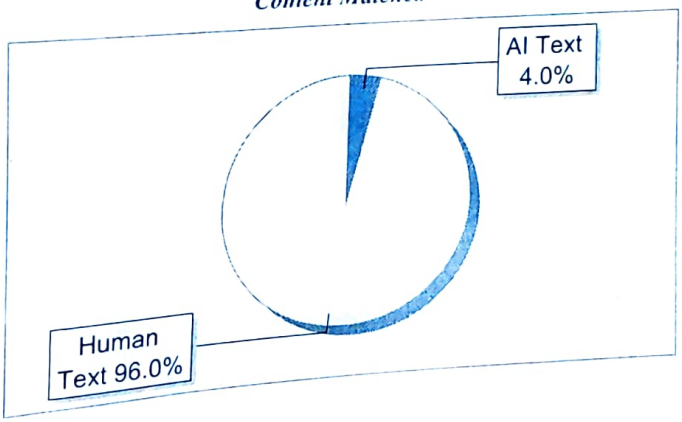

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